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# ANALYTICAL REFERENCE SERVICE. REPORT ON WATER TRACE-ELEMENTS NO. 1

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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PB 227 854

# Report of
# ANALYTICAL REFERENCE SERVICE
# WATER TRACE-ELEMENTS No. 1

Conducted by the

Analytical Reference Service

TRAINING PROGRAM

U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Public Health Service
Bureau of State Services
Division of Water Supply and Pollution Control

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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Springfield VA 22151

## ANALYTICAL REFERENCE SERVICE

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# FOREWORD

The Analytical Reference Service is conducted by the Public Health Service at the Robert A. Taft Sanitary Engineering Center to provide a means of evaluating laboratory methods in the field of environmental sciences and engineering. Membership includes federal, state, and municipal agencies, industries, universities, consulting firms, and foreign agencies. Cooperative studies by member organizations, through analysis of identical samples of environmental media and critical review of methodology, provide the mechanism for:

1. Statistical evaluation of procedures, including precision and accuracy.

2. Comparison of analytical procedures and results between laboratories having similar responsibilities.

3. Exchange of information regarding weaknesses of currently approved methods.

4. Further development of methods or entirely new approaches.

5. Broad-scale evaluation of new analytical methods.

While largely directed toward the chemical examination of water, the studies have been broadened gradually to include radioactivity, air pollution, and milk and food contamination. Samples are designed and prepared to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the staff of ARS, the membership, and consultants. Notice of a study is forwarded to each member with information regarding the qualitative makeup of the sample and special details regarding its handling.

A portion of the sample is shipped to the interested members with accompanying data forms which provide space for numerical analytical values and a narrative critique of the procedures used. The participating agencies are urged to comment on the methods, difficulties, modifications, sources of error, and other factors. Results are requested within sixty days from receipt of the sample.

The results and comments of each study are compiled, as in the accompanying report in which 31 member laboratories contributed data. Experience indicates that a repeat study produces a sizeable increase in the number of participants. For example, in the 1956 water-minerals study, 19 agencies participated; in the 1958 study, 31 member agencies participated; 59 agencies cooperated in the 1961 study.

The final report for the recent water-metals study is being prepared. A report of the milk sample for the determination of DDT by a specified method is being written. A sample for the determination of strontium-90 in water has been prepared and will be shipped in the near future. An $SO_2$ in Air study is being planned. Selection of these studies was guided by a poll of member interests. It will continue to serve as a basis for future studies. The steadily increasing membership, 131 agencies, strongly indicates the broad interest in and need for this type of service.

H P Kramer

H. P. Kramer
Chief, Training Program

## STUDIES ON WHICH REPORTS HAVE BEEN COMPLETED

| | |
|---|---|
| Water-Minerals | Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium. Studies were completed in 1956, 1958 and 1961. |
| Water-Metals | Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. A study was completed in 1957 and the report on a second study will be distributed in the near future. |
| Water-Fluoride | Fluoride in the presence and absence of interferences with and without distillation, using a specified procedure. Studies were completed in 1958 and 1961. |
| Water-Radiological | Gross beta and gamma activity. Studies were completed in 1959 and 1961. |
| Water-Surfactant | Surfactant in various waters. A study was completed in 1959. |
| Water-Oxygen Demand | Biochemical oxygen demand and chemical oxygen demand. A study was completed in 1960. |
| Air-Inorganics | Chloride, sulfate, fluoride and nitrate in aqueous solution and on glass fiber hi-vol filter mats. A study was completed in 1958. |
| Air-Lead | Filter paper tape impregnated with lead. A study was completed in 1961. |

## STUDIES IN PROGRESS

| | |
|---|---|
| Milk-Determination of DDT Residues | |
| Water-$Sr^{90}$ | To be shipped April 16, 1962. |

## PARTICIPANTS IN THIS STUDY

Arizona State Department of Health
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Idaho Department of Health
Louisiana State Board of Health
Maryland State Department of Health
Montana State Board of Health
New Jersey Department of Health
New Mexico State Department of Public Health
New York State Department of Health
Ohio State Department of Health
Pennsylvania Department of Health
Tennessee Stream Pollution Control Board
Vermont State Department of Health
Los Angeles Department of Water and Power
Los Angeles County Flood Control District
Los Angeles Department of Public Works (Hyperion Treatment Plant)
Chicago Department of Water and Sewers
Omaha Metropolitan Utilities District
U. S. Army Environmental Hygiene Agency, Maryland
U. S. Dept. of the Interior, Geological Survey, Sacramento, California
U. S. Dept. of the Interior, Geological Survey, Denver, Colorado
U. S. Dept. of the Interior, Geological Survey, Columbus, Ohio
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
California Water Service Company, San Jose, California
Hagan Chemicals & Controls, Inc., Pittsburgh, Pennsylvania
Kennecott Copper Corporation, Salt Lake City, Utah
Radiation Detection Company, Palo Alto, California
Sandia Corporation, Sandia Base, Albuquerque, New Mexico

# WATER TRACE-ELEMENTS No. 1

## PURPOSE OF STUDY

This study was the first reference sample containing arsenic, boron, selenium, and beryllium. Thirty-one agencies participated. It was designed at the request of Analytical Reference Service members who recognized a need for evaluation of current procedures and for comparison of individual laboratory results. It has been recognized that the presence of these trace elements in water have potential health and economic significance. The study served also as a survey of methods currently employed on a national basis. Each element in the sample was analyzed by a number of methods, permitting comparative evaluations.

## PREPARATION OF SAMPLE

Substrate: Distilled water passed through a deionizing column.

Chemicals: ACS Reagent Grade, taken from newly opened bottles.

Composition: Sample Water Trace-Elements No. 1, consisted of 180 liters of substrate containing carefully measured portions of selenium dioxide, beryllium sulfate, boric acid, and dibasic sodium acid arsenate to give the following concentrations:

| | |
|---|---|
| Arsenic | 0.05 mg/l |
| Boron | 0.18 mg/l |
| Beryllium | 0.40 mg/l |
| Selenium | 0.05 mg/l |

## TREATMENT OF THE DATA

The participating agencies reported a total of 253 analytical results based on measurements made in triplicate. For convenience, the mean of the replicates for each determination from each agency is tabulated with the average deviation from the individual replicate results. Shown also is the average deviation of the replicates from the amount added. The multiplicity of references cited for each analysis would make statistical evaluation meaningless if each reference were treated as a separate method. The various procedures, therefore, have been grouped according to the basic reactions and slight modifications in technique have not been considered in the evaluation. The references cited by participants are noted in Tables 1 - 4. But in the narrative, reference is made to the basic procedure that was most commonly used or that best detailed the method.

The standard deviations were calculated by using the difference between

the separate results and the known amount of material added. All reported values were retained regardless of the magnitude of deviation. The standard deviations reported here are a function of concentration. If the amount of material being measured were halved or doubled, the standard deviation probably would vary depending on the changes required or affected by the new concentration.

To relate the accuracy of the methods more directly to the agencies performing the determinations, the term "50% range" is used. This range is defined as the maximum deviation from the amount of material added for the more accurate half (50%) of all results for each measurement. For example, on the arsenic determination the range for 27 laboratories was ± 0.15 mg/l, but at least 14 (50%) laboratories reported values within ± 0.01 mg/l of the true value. Early in this program, consultation with members produced agreement that a 50% range would be a reasonable goal for accuracy.

Since it was requested, in the instruction sheet accompanying the sample, that results be reported to the nearest hundredth mg/l, those values reported to three decimal places were rounded off for uniformity, using the rule in Standard Methods.[1] Several averages were treated in the same manner. Since too few comments were offered to justify a separate section in this report, they will be noted briefly in the appropriate discussions. Average reported values are shown in the bar charts and the different analytical methods employed are identified.

## DISCUSSION AND COMMENTS

### ARSENIC (0.05 mg/l)

Twenty-seven members performed the arsenic determination. Of these, 13 used a silver diethyldithiocarbamate procedure,[2] 9 used a heteropoly molybdenum blue procedure,[1] and the remaining 5 used a Gutzeit method.[1] Approximately equal precision was obtained by all three methods, but much greater accuracy was obtained from the silver diethyldithiocarbamate procedure. The bar charts show that the Gutzeit method tends to produce high results while the opposite is true for the other two methods.

All but three of the results were within one standard deviation. The average of all results was 0.05 mg/l and the median value was 0.04 mg/l.

For the silver diethyldithiocarbamate procedures, the standard deviation was ± 0.013 mg/l; the heteropoly blue was ± 0.025 mg/l; and the Gutzeit method was ± 0.060 mg/l.

Participants commented that the silver diethyldithiocarbamate procedure was quicker, simpler, and more sensitive than the heteropoly blue method, and in addition is very reproducible. One participant commented that it was necessary to concentrate the sample tenfold to obtain satisfactory results.

While the silver diethyldithiocarbamate procedure appears to give slightly low results, the accuracy

shown by all parameters used in Table 5, together with the simplicity and speed of the determination, indicates that it is the superior method.

## SUMMARY OF ARSENIC ANALYSIS

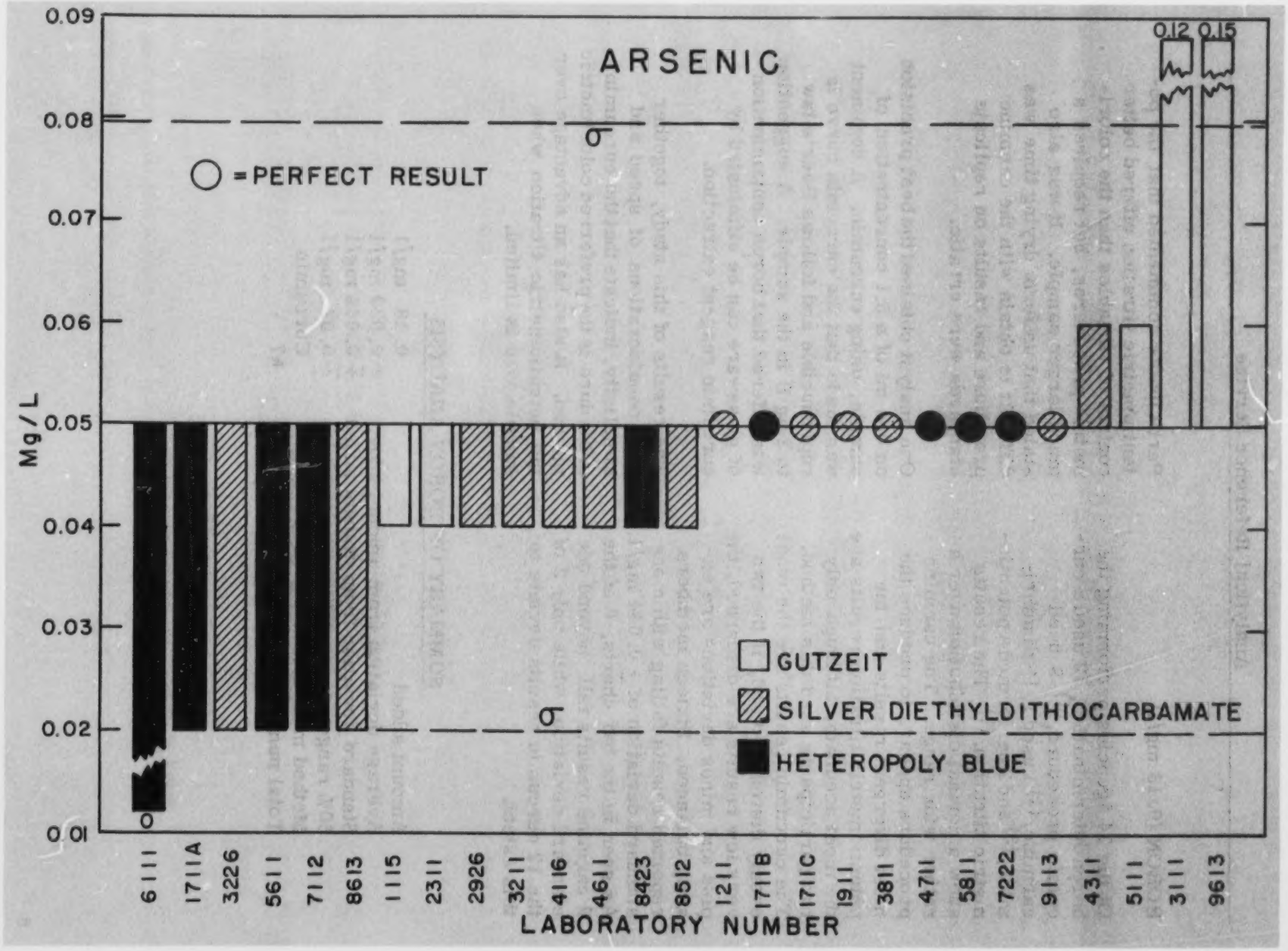
| | |
|---|---|
| Amount added | 0.05 mg/l |
| Average deviation from amount added | ± 0.018 mg/l |
| Standard deviation from amount added | ± 0.030 mg/l |
| 50% range | ± 0.01 mg/l |
| Method most commonly used | Silver diethyl-dithiocarbamate |
| Total number of analyses | 80 |

Table 1. ARSENIC (Amount added - 0.05 mg/l)

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 1115 | 0.05<br>0.03<br>0.05 | 0.04 | 0.010 | 0.007 | Gutzeit[1] |
| 1211 | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Silver DDC[2] |
| 1711A | 0.02<br>0.02<br>0.02 | 0.02 | 0 | 0.030 | Heterop. Blue[1][10] |
| 1711B | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Heterop. Blue[1] |
| 1711C | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Silver DDC[2] |
| 1911 | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Silver DDC[2] |
| 2311 | 0.04<br>0.04<br>---- | 0.04 | 0 | 0.010 | Gutzeit |
| 2926 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Silver DDC[11] |
| 3111 | 0.13<br>0.12<br>0.12 | 0.12 | 0.003 | 0.073 | Gutzeit[1] |
| 3211 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Silver DDC[12] |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs. | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 3226 | 0.03<br>0.02<br>0.02 | 0.02 | 0.003 | 0.027 | Silver DDC[2] |
| 3811 | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Silver DDC[2] |
| 4116 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Silver DDC |
| 4311 | 0.06<br>0.06<br>0.05 | 0.06 | 0.003 | 0.007 | Silver DDC[12] |
| 4611 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Silver DDC[2] |
| 4711 | 0.05<br>0.06<br>0.05 | 0.05 | 0.003 | 0.003 | Heterop. Blue[1] |
| 5111 | 0.06<br>0.06<br>0.06 | 0.06 | 0 | 0.010 | Gutzeit[1] |
| 5611 | 0.02<br>0.02<br>0.02 | 0.02 | 0 | 0.030 | Heterop. Blue |
| 5811 | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Heterop. Blue[1] |
| 6111 | 0.00<br>0.00<br>0.00 | 0.00 | 0 | 0.050 | Heterop. Blue[1] |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 7112 | 0.02<br>0.02<br>0.02 | 0.02 | 0 | 0.030 | Heterop. Blue[13] |
| 7222 | 0.04<br>0.04<br>0.06 | 0.05 | 0.010 | 0.010 | Heterop. Blue[1] |
| 8423 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Heterop. Blue[1] |
| 8512 | 0.05<br>0.04<br>0.04 | 0.04 | 0.003 | 0.007 | Silver DDC[2] |
| 8613 | 0.02<br>0.02<br>0.02 | 0.02 | 0 | 0.030 | Silver DDC[14] |
| 9113 | 0.05<br>0.05<br>0.05 | 0.05 | 0 | 0 | Silver DDC[15] |
| 9613 | 0.15<br>0.15<br>0.15 | 0.15 | 0 | 0.100 | Gutzeit[1] |


ARSENIC
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
Mg/L
0.12
0.15
○ = PERFECT RESULT
σ
σ
GUTZEIT
SILVER DIETHYLDITHIOCARBAMATE
HETEROPOLY BLUE
6111
1711A
3226
5611
7112
8613
1115
2311
2926
3211
4116
4611
8423
8512
1211
1711B
1711C
1911
3811
4711
5811
7222
9113
4311
5111
3111
9613
LABORATORY NUMBER

BORON (0.18 mg/l)

Of the 24 agencies performing the boron determination, 12 used a curcumin procedure, [1] 9 used carmine, [1] 1 used 1, 1'-dianthrimide, [3] and 2 performed a potentiometric titration. [1] The results show a normal distribution over a rather wide range. The carmine procedure appears to produce the most divergent results and the potentiometric titration results are the most accurate, although only two participants used this method. The curcumin results are the most evenly distributed and, if the two very low results are discarded, the plus and minus deviations are exactly balanced. Sixteen members reported results falling within one standard deviation of $\pm$ 0.044 mg/l. As seen in the bar charts, 6 of the 9 carmine results fall beyond one standard deviation, while only 2 of the 12 curcumin results deviate to this extent.

Participants commented that the potentiometric titration offered better control of variables than the colorimetric procedures, but requires a much larger sample. It was also stated that uniform drying time was difficult to obtain with the carmine procedure and results on replicate standards were erratic.

One analyst obtained the best precision on one ml of a 5:1 concentration of sample, using curcumin. A comment was made that the curcumin curve is reproducible and follows Beer's law to 2 µg B in the sample. A suggestion was offered that boron contamination of glassware can be eliminated by curcumin reagent extraction.

The results of this study, together with considerations of speed and simplicity, indicate that the curcumin procedure is the preferred colorimetric method. It also has an advantage over the potentiometric titration when sample size is limited.

SUMMARY OF BORON ANALYSIS

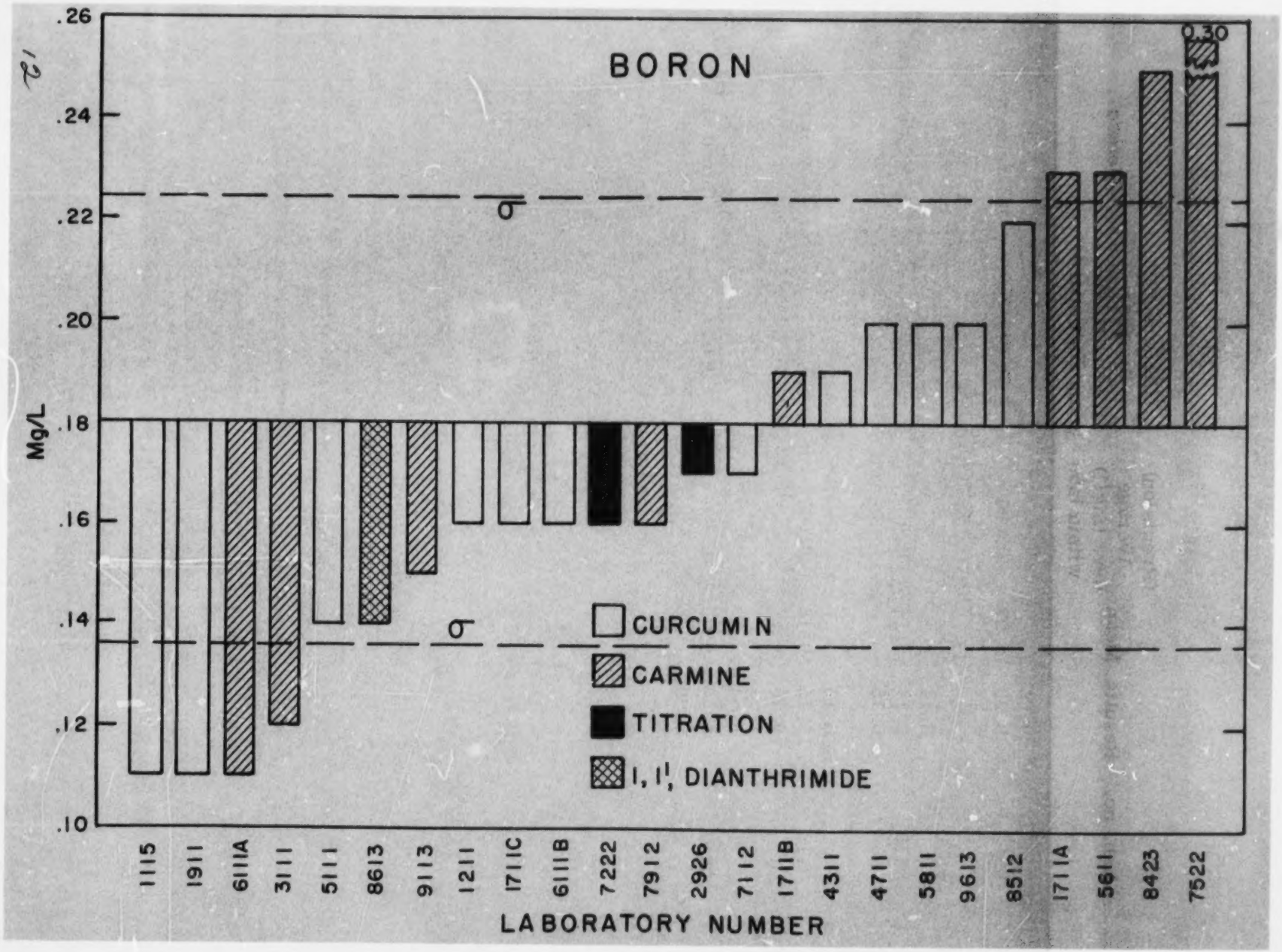
| | |
|---|---|
| Amount added | 0.18 mg/l |
| Average deviation from amount added | $\pm$ 0.039 mg/l |
| Standard deviation from amount added | $\pm$ 0.044 mg/l |
| 50% range | $\pm$ 0.02 mg/l |
| Method most commonly used | Curcumin |
| Total number of analyses | 67 |

Table 2. BORON (Amount added - 0.18 mg/l)

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 1115 | 0.11<br>----<br>---- | 0.11 | 0 | 0.070 | Curcumin(1) |
| 1211 | 0.18<br>0.15<br>0.15 | 0.16 | 0.013 | 0.020 | Curcumin(1) |
| 1711A | 0.23<br>0.24<br>0.21 | 0.23 | 0.010 | 0.047 | Carmine(1) |
| 1711B | 0.24<br>0.18<br>0.16 | 0.19 | 0.030 | 0.027 | Carmine |
| 1711C | 0.17<br>0.15<br>0.15 | 0.16 | 0.010 | 0.023 | Curcumin(1) |
| 1911 | 0.11<br>0.11<br>0.11 | 0.11 | 0 | 0.070 | Curcumin(1) |
| 2926 | 0.18<br>0.17<br>0.17 | 0.17 | 0.003 | 0.007 | Potentiometric(1) Titration |
| 3111 | 0.12<br>0.12<br>---- | 0.12 | 0 | 0.060 | Carmine(1) |
| 4311 | 0.20<br>0.20<br>0.18 | 0.19 | 0.010 | 0.013 | Curcumin(1) |
| 4711 | 0.18<br>0.18<br>0.23 | 0.20 | 0.023 | 0.017 | Curcumin(1) |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 5111 | 0.14<br>0.14<br>0.13 | 0.14 | 0.003 | 0.043 | Curcumin[1] |
| 5611 | 0.23<br>0.23<br>0.24 | 0.23 | 0.003 | 0.053 | Carmine |
| 5811 | 0.21<br>0.19<br>0.20 | 0.20 | 0.007 | 0.020 | Curcumin[1] |
| 6111A | 0.12<br>0.12<br>0.10 | 0.11 | 0.010 | 0.067 | Carmine[1] |
| 6111B | 0.14<br>0.14<br>0.19 | 0.16 | 0.023 | 0.030 | Curcumin[1] |
| 7112 | 0.16<br>0.18<br>---- | 0.17 | 0.010 | 0.010 | Curcumin[1] |
| 7222 | 0.15<br>0.17<br>0.17 | 0.16 | 0.010 | 0.017 | Potentiometric[1] Titration |
| 7522 | 0.29<br>0.30<br>0.30 | 0.30 | 0.003 | 0.117 | Carmine[16] |
| 7912 | 0.14<br>0.16<br>0.18 | 0.16 | 0.013 | 0.020 | Carmine[1] |
| 8423 | 0.25<br>0.25<br>0.26 | 0.25 | 0.003 | 0.073 | Carmine[1] mod. by acid evap. @ 105°C |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 8512 | 0.25<br>0.20<br>---- | 0.22 | 0.025 | 0.045 | Curcumin[1] |
| 8613 | 0.14<br>0.14<br>0.15 | 0.14 | 0.003 | 0.037 | 1,1', dianthri-[3] mide |
| 9113 | 0.14<br>0.15<br>0.16 | 0.15 | 0.007 | 0.030 | Carmine[17] |
| 9613 | 0.20<br>0.20<br>0.20 | 0.20 | 0 | 0.020 | Curcumin[1] |


BORON
.26
.24
.22
.20
.18
.16
.14
.12
.10
Mg/L
CURCUMIN
CARMINE
TITRATION
I, I', DIANTHRIMIDE
1115
1911
6111A
3111
5111
8613
9113
1211
1711C
6111B
7222
7912
2926
7112
1711B
4311
4711
5811
9613
8512
1711A
5611
8423
7522
LABORATORY NUMBER

SELENIUM (0.05 mg/l)

Twenty-one members performed the selenium analysis. The Cheng[4] colorimetric procedure using 3,3' diaminobenzidine, with various modifications, was employed by 12 analysts. Modifications included concentration of the sample by evaporation, addition of EDTA to complex interfering metals, and removal of interferences by ion exchange.[6] Three agencies reported using a colored sol[1] procedure, and six reported using the AWWA subcommittee procedure.[5] The latter method is similar to the Cheng procedure but involves a step to oxidize all selenium to the selenate form, and then a controlled reduction to the selenite form. The AWWA subcommittee procedure produced results with the best precision and accuracy. Results from all methods show normal distribution with six perfect results.

It is evident that good results may be obtained with any of these procedures, but this study indicates that the AWWA subcommittee method is superior. This method has the added advantage of being able to measure the selenate form as well as the selenite.

The comment was offered that the colorimetric curve reproduces well but the reagent is expensive and very unstable.

SUMMARY OF SELENIUM ANALYSIS

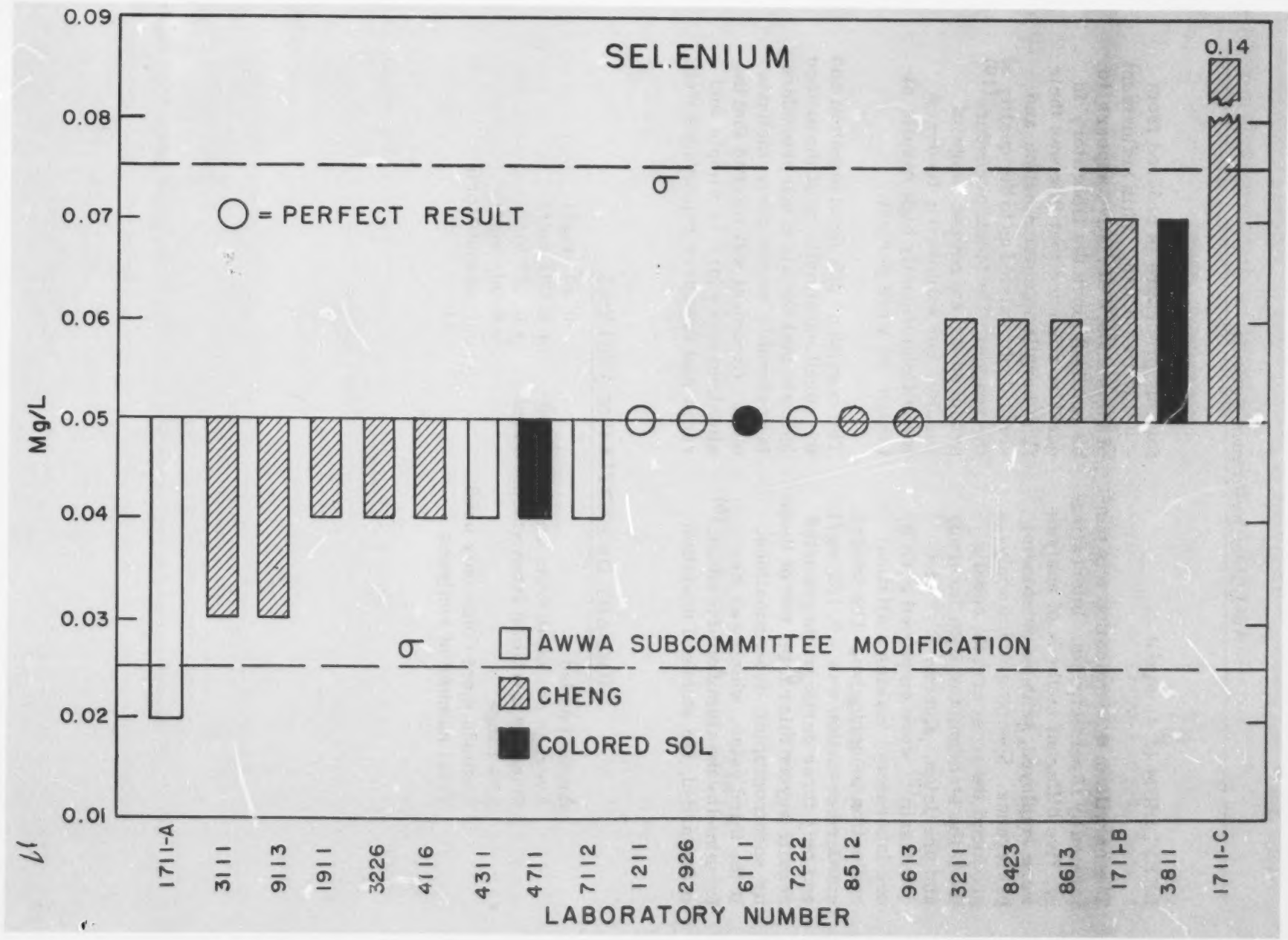
| | |
|---|---|
| Amount added | 0.05 mg/l |
| Average deviation from amount added | $\pm$ 0.015 mg/l |
| Standard deviation from amount added | $\pm$ 0.025 mg/l |
| 50% range | $\pm$ 0.01 mg/l |
| Method most commonly used | Cheng |
| Total number of analyses | 62 |

Table 3. SELENIUM (Amount added - 0.05 mg/l)

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 1211 | 0.05<br>0.05<br>0.04 | 0.05 | 0.003 | 0.003 | AWWA[5] Subcommittee |
| 1711A | 0.02<br>0.03<br>0.02 | 0.02 | 0.003 | 0.027 | AWWA[5] Subcommittee |
| 1711B | 0.07<br>0.07<br>0.07 | 0.07 | 0 | 0.020 | Cheng[4] |
| 1711C | 0.14<br>0.15<br>0.14 | 0.14 | 0.003 | 0.093 | Cheng[4] |
| 1911 | 0.04<br>0.04<br>0.05 | 0.04 | 0.003 | 0.007 | Cheng[4] |
| 2926 | 0.04<br>0.05<br>0.05 | 0.05 | 0.003 | 0.003 | AWWA[5] Subcommittee |
| 3111 | 0.03<br>0.03<br>0.04 | 0.03 | 0.003 | 0.017 | Cheng |
| 3211 | 0.06<br>0.04<br>0.08 | 0.06 | 0.013 | 0.017 | Cheng[4] |
| 3226 | 0.04<br>0.04<br>0.05 | 0.04 | 0.003 | 0.007 | Cheng[6] |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 3811 | 0.07<br>0.07<br>0.07 | 0.07 | 0 | 0.020 | Colored Sol[18] |
| 4116 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | Cheng |
| 4311 | 0.04<br>0.04<br>0.04 | 0.04 | 0 | 0.010 | AWWA[5] Subcommittee |
| 4711 | 0.03<br>0.04<br>0.05 | 0.04 | 0.007 | 0.010 | Colored Sol[1] |
| 6111 | 0.07<br>0.03<br>---- | 0.05 | 0.020 | 0.020 | Colored Sol[1] |
| 7112 | 0.05<br>0.04<br>0.04 | 0.04 | 0.003 | 0.007 | AWWA Subcommittee |
| 7222 | 0.05<br>0.04<br>0.05 | 0.05 | 0.003 | 0.003 | AWWA Subcommittee |
| 8423 | 0.06<br>0.06<br>0.07 | 0.06 | 0.003 | 0.013 | Cheng[4] |
| 8512 | 0.05<br>0.05<br>0.04 | 0.05 | 0.003 | 0.003 | Cheng[4] |

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs. | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 8613 | 0.06<br>0.06<br>0.05 | 0.06 | 0.003 | 0.007 | Cheng[6] |
| 9113 | 0.03<br>0.03<br>0.03 | 0.03 | 0 | 0.020 | Cheng[6] |
| 9613 | 0.05<br>0.05<br>0.06 | 0.05 | 0.003 | 0.003 | Cheng[4] |


SELENIUM
0.14
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
Mg/L
σ
○ = PERFECT RESULT
σ
AWWA SUBCOMMITTEE MODIFICATION
CHENG
COLORED SOL
1711-A
3111
9113
1911
3226
4116
4311
4711
7112
1211
2926
6111
7222
8512
9613
3211
8423
8613
1714B
3811
1711-C
LABORATORY NUMBER

BERYLLIUM (0.40 mg/l)

The beryllium determination was performed by 16 participants. Interestingly, five different methods of analysis were employed, with no outstanding preference. Spectrographic analysis produced the most erratic results from the standpoint of both accuracy and precision. Curcumin[1] and quinizarin[8] were employed each by one laboratory, making statistical evaluation inconclusive. The overall standard deviation was ± 0.122 mg/l and only three participants reported results beyond this range, two of these by spectrographic determinations. If the third value, which was determined by the aluminon procedure,[9] is discarded, the standard deviation for this procedure is reduced from ± 0.130 to ± 0.015. This refinement of the standard deviation appears to be justified since the laboratory in question reported that this was their first beryllium determination and some doubt existed as to the quality of the reagent. The Morin procedure[10] produced the narrowest range of results, but exhibited a tendency toward significantly high results although two were perfect.

The results of this determination and the speed and simplicity of the method indicate that the aluminon procedure is preferable to the other methods used. Comment was offered that the aluminon procedure is simple and rapid and the curve reproduces well.

SUMMARY OF BERYLLIUM ANALYSIS

| | |
|---|---|
| Amount added | 0.40 mg/l |
| Average deviation from amount added | ± 0.091 mg/l |
| Standard deviation from amount added | ± 0.122 mg/l |
| 50% range | ± 0.06 mg/l |
| Methods most commonly used | Aluminon and Morin |
| Total number of analyses | 44 |

Table 4. BERYLLIUM (Amount added - 0.40 mg/l)

| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 1711C | 0.32<br>0.20<br>0.42 | 0.31 | 0.077 | 0.100 | Spectrograph |
| 1911 | 0.39<br>0.38<br>0.38 | 0.38 | 0.003 | 0.017 | Aluminon[9] |
| 3111 | 0.07<br>0.07<br>---- | 0.07 | 0 | 0.330 | Aluminon[9] |
| 3416 | 0.44<br>0.48<br>0.45 | 0.46 | 0.017 | 0.057 | Morin |
| 3816 | 0.40<br>0.40<br>0.40 | 0.40 | 0 | 0 | Morin[19] |
| 4711 | 0.65<br>0.70<br>0.60 | 0.65 | 0.033 | 0.250 | Spectrograph |
| 5111 | 0.34<br>0.35<br>0.35 | 0.35 | 0.003 | 0.053 | Quinizarin[8]<br>2-sulfonic acid |
| 5611 | 0.50<br>0.50<br>0.50 | 0.50 | 0 | 0.100 | Morin[10] |
| 5811 | 0.41<br>0.39<br>0.40 | 0.40 | 0.007 | 0.007 | Morin[19] |
| 6111 | 0.50<br>0.50<br>---- | 0.50 | 0 | 0.100 | Curcumin[7] |



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| Lab. no. | Results | Mean | (Precision) Average dev. (mg/l) within labs | (Accuracy) Average dev. (mg/l) from am't added | Method |
|---|---|---|---|---|---|
| 7112 | 0.42<br>0.45<br>0.50 | 0.46 | 0.030 | 0.057 | Spectrograph |
| 7222 | 0.54<br>0.45<br>0.56 | 0.52 | 0.043 | 0.117 | Morin[10] |
| 8423 | 0.17<br>----<br>---- | 0.17 | 0 | 0.230 | Spectrograph[20] |
| 8512 | 0.39<br>0.40<br>0.40 | 0.40 | 0.003 | 0.003 | Aluminon[9] |
| 9113 | 0.38<br>0.38<br>0.39 | 0.38 | 0.003 | 0.017 | Aluminon[21] |
| 9613 | 0.38<br>0.39<br>0.39 | 0.39 | 0.003 | 0.013 | Aluminon[9] |

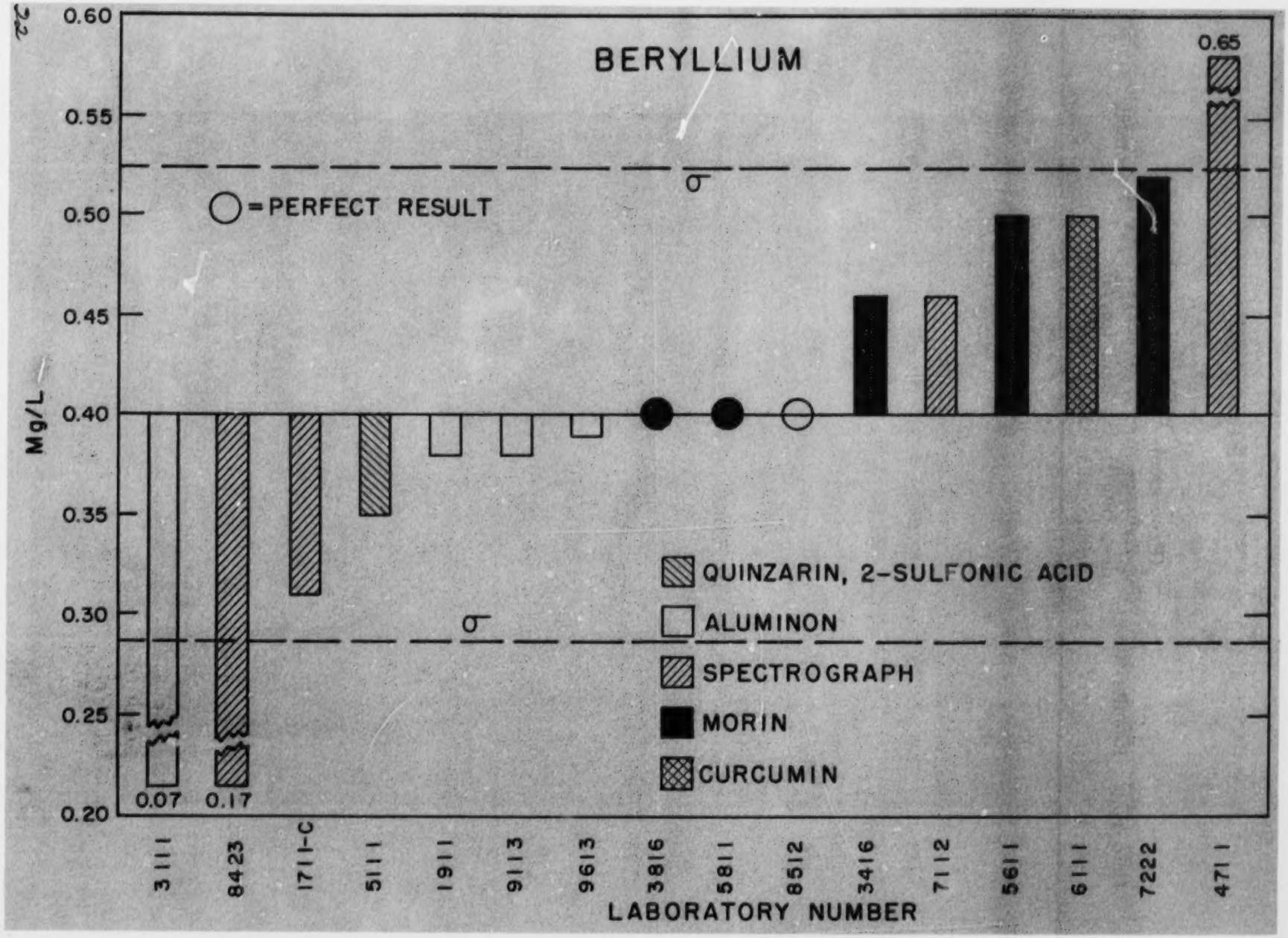
22
BERYLLIUM
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
Mg/L
○ = PERFECT RESULT
σ
σ
0.65
0.07
0.17
QUINZARIN, 2-SULFONIC ACID
ALUMINON
SPECTROGRAPH
MORIN
CURCUMIN
3111
8423
1711-C
5111
1911
9113
9613
3816
5811
8512
3416
7112
5611
6111
7222
4711
LABORATORY NUMBER

Table 5. SUMMARY OF DATA

| | ARSENIC | | | | BORON | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | All methods | Gutzeit | Silver DDC | Heter, Blue | All methods | Curcumin | Carmine | Potentio. Titr. | 1, 1'-dianth. |
| Am't. added, mg/l | 0.05 | 0.05 | 0.05 | 0.05 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 |
| No. of analyses | 80 | 14 | 39 | 27 | 67 | 32 | 26 | 6 | 3 |
| Mean of av. results | 0.05 | 0.08 | 0.04 | 0.03 | 0.18 | 0.17 | 0.19 | 0.16 | 0.14 |
| Median of av. results | 0.04 | 0.06 | 0.04 | 0.04 | 0.16 | 0.16 | 0.19 | 0.16 | 0.14 |
| Range of av. results | 0.00-0.15 | 0.04-0.15 | 0.02-0.06 | 0.00-0.05 | 0.11-0.30 | 0.11-0.22 | 0.11-0.30 | 0.16-0.17 | 0.14 |
| Av. deviation | ± 0.018 | ± 0.040 | ± 0.008 | ± 0.018 | ±0.039 | ±0.032 | ±0.055 | ±0.012 | ±0.037 |
| Standard deviation | ± 0.030 | ± 0.060 | ± 0.013 | ± 0.025 | ±0.044 | ±0.038 | ±0.064 | ±0.015 | ±0.037 |
| Av. deviation within labs | ± 0.001 | ± 0.003 | ± 0.001 | ± 0.001 | ±0.010 | ±0.012 | ±0.009 | ±0.007 | ±0.003 |
| No. of users | 27 | 5 | 13 | 9 | 24 | 12 | 9 | 2 | 1 |

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| | SELENIUM | | | | BERYLLIUM | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | All methods | AWWA Subcommittee | Colored Sol | Cheng | All methods | Aluminon | Spectro-graph | Morin | Curcumin | Quinizarin |
| Am't added, mg/l | 0.05 | 0.05 | 0.05 | 0.05 | 0.40 | 0.40 | 0.40 | 0.40 | 0.40 | 0.40 |
| No. of analyses | 62 | 18 | 8 | 36 | 44 | 14 | 10 | 15 | 2 | 3 |
| Mean of av. results | 0.05 | 0.04 | 0.05 | 0.06 | 0.40 | 0.32 | 0.40 | 0.46 | 0.50 | 0.35 |
| Median of av. results | 0.05 | 0.04 | 0.05 | 0.05 | 0.40 | 0.37 | 0.38 | 0.46 | 0.50 | 0.35 |
| Range of av. results | 0.02-0.14 | 0.02-0.05 | 0.04-0.07 | 0.03-0.14 | 0.07-0.65 | 0.07-0.40 | 0.17-0.65 | 0.40-0.52 | 0.50 | 0.35 |
| Av. deviation | ±0.015 | ±0.009 | ±0.016 | ±0.018 | ±0.091 | ±0.076 | ±0.159 | ±0.056 | ±0.100 | ±0.053 |
| Standard deviation | ±0.025 | ±0.013 | ±0.019 | ±0.030 | ±0.122 | ±0.130 | ±0.184 | ±0.079 | ±0.100 | ±0.054 |
| Av. deviation within labs | ±0.004 | ±0.002 | ±0.009 | ±0.003 | ±0.014 | ±0.002 | ±0.035 | ±0.013 | ±0.00 | ±0.003 |
| No. of users | 21 | 6 | 3 | 12 | 16 | 5 | 4 | 5 | 1 | 1 |

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